

THE WETTING CHARACTERISTICS OF GALENA

BY
GEORGE B. HATCH

DISSERTATION
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
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THE WETTING CHARACTERISTICS OF GALENA

Recent work has shown that the free surface energy of a solid, hence its wetting characteristics, may be altered much more easily than had previously been supposed. In view of this fact, it is apparent that the pretreatment of a solid surface must be carefully controlled if significant values of its wetting properties are to be obtained. It seems probable that failure to consider carefully the exact surface condition of the solid accounts for the fact that existing data on wetting properties of solids show such an outstanding lack of agreement.

In recent years much work has been done in an effort to determine the wetting characteristics of galena, such information being highly desirable in connection with the ore flotation industry. The angle of contact of water on galena has been used as a measure of its wetting characteristics and there has been a surprising lack of agreement in the data which have been obtained. Sulman (11) found the advancing water-air angle for one sample of galena to be 73° , and for another 70° , the respective receding angles being 35° and 41.6° . Langmuir (9) obtained an angle of 86° , while Coghill and Anderson (5) found angles from 45° to 60° . These angles were apparently advancing angles. In none of these cases are we certain as to the exact condition of the surfaces. Wark and Cox (12) found an "equilibrium" angle of zero degrees for water upon a galena plate cleaved under water, the angle they measured being in reality a receding angle. They found that a finite angle was formed if the galena was cleaved in air and assumed that the difference was caused by contamination. Reh-binder, Lipetz, Remskaja, and Taubman (10) obtained a 47° advancing and a zero receding angle for water upon freshly cleaved galena.

In view of the lack of agreement in the literature concerning galena, we felt that a study of this solid should yield information of value. Our primary object was to determine the wetting characteristics of the galena surface by measurement of contact angles and to study the factors which might influence such measurements. This objective led to the investigation of the following factors:

1. Different methods for measuring contact angles.
2. The phenomenon of "hysteresis" of the angle of contact, i.e., the relation of the advancing to the receding angles.

3. The effect of the pretreatment of the solid surface upon the angle of contact.

SIGNIFICANCE OF CONTACT ANGLES

The degree of wetting or adhesion tension of a liquid against a solid has been defined as that change in free surface energy which occurs when a solid-air surface is replaced by a solid-liquid interface. The adhesion tension is related to the contact angle as follows:

$A_{13} = S_3 \cos \theta_{13}$ (8), where A_{13} represents the adhesion tension, liquid against solid, S_3 the surface tension of the liquid, and $\cos \theta_{13}$ the cosine of the contact angle between liquid and solid in air.

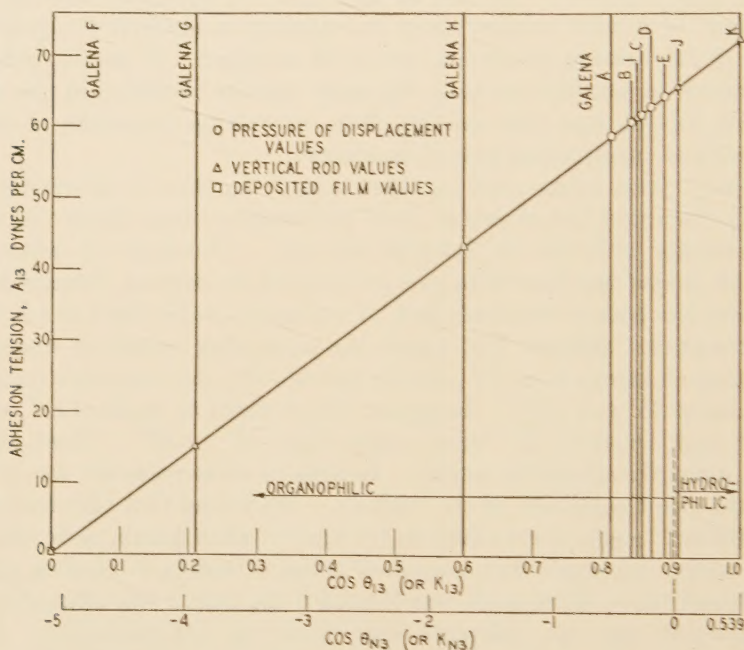


FIG. 1

It has been found from numerous studies in our laboratory that solids on which water gives a contact angle greater than approximately 25° ($\cos \theta_{13} = 0.90$) are organophilic in nature, i.e., they are preferentially wetted by organic liquids, while those giving an angle less than 25° are hydrophilic (1) and are preferentially wetted by water. The change in wetting properties progresses with change in contact angle (or $\cos \theta_{13}$).

In the present paper we shall express the wetting characteristics of the different solids in terms of the cosine of the solid-water-air contact angle, $\cos \theta_{13}$ (or K_{13})—and shall consider that the solids are organophilic when

$\cos \theta_{13} < 0.90$ and that they are hydrophilic when $\cos \theta_{13} > 0.90$. Straight line graphs, of slope S_3 , may be made by plotting A_{13} against $\cos \theta_{13}$ (see figure 1). The position of a solid on the horizontal, $\cos \theta_{13}$, axis will show the relative degree of organophilic or hydrophilic nature of the solid.

QUALITATIVE WETTING TESTS

Preliminary studies on the wetting characteristics of galena powder yielded some rather surprising results. It was found that if the powdered material was first wetted with water, an organic liquid could not readily be stirred into the resulting paste, while if it was first wetted with an organic liquid, water could not readily be stirred into it. When the powder was packed into a U-tube, or a displacement pressure cell, half of the powder being wetted with the organic liquid and the remainder with water, no displacement of one liquid by the other occurred. To cause movement of the interface in either direction it was necessary to apply an external force. Once this force was removed, the line of contact of the interface with the solid appeared to remain fixed.

When these qualitative tests were repeated, using carbon or silica, entirely different results were obtained; the organic liquid would completely displace water from the carbon, and water would completely displace the organic liquid from the silica. In contrast to the behavior of these two solids, galena appeared to be preferentially wetted by either liquid, depending upon which was first present. Thus, if the galena was first wetted with water it behaved similarly to the hydrophilic silica, whereas if it was first wetted with the organic liquid it behaved as the organophilic carbon. It should be stressed that this wetting produced no permanent change of the surface. If the powder was dried after being wetted with water or with a volatile organic liquid, it behaved exactly as the freshly prepared material.

MATERIALS

Liquids

Liquids used in this investigation were water, benzene, *n*-butyl acetate, and α -bromonaphthalene. All were carefully purified, and their densities, surface tensions, and interfacial tensions (against water) agreed, within the limits of experimental error, with the generally accepted values. The following surface tension and interfacial tension values respectively (for 25°C.) were used in our calculations: water, 72.08; benzene, 28.22 and 34.00; *n*-butyl acetate, 24.06 and 13.17; α -bromonaphthalene, 44.00 and 41.57.

Solids

Galena in the form of powder, plates, rods, and films was used. In the measurement of contact angles by the pressure of displacement method,

TABLE 1

Contact angle data for galena by the displacement pressure method (advancing air-water-solid contact angles)

$t = 25^{\circ}\text{C.} \pm 0.10^{\circ}$; r (pore radius) $= 8.18 \times 10^{-4}$ cm.

SOLID	DISPLACEMENT PRESSURE	θ_{13} (ADVANCING)	$\cos \theta_{13}$	A_{13}
	grams per sq. cm.			
Galena A.....	146	35.4°	0.815	58.7
Galena B.....	151	32.5°	0.843	60.7
Galena C.....	154	31.1°	0.856	61.7
Galena D.....	156	29.5°	0.870	62.7
Galena E.....	160	27.1°	0.891	64.2

The receding contact angles for the different samples of galena were all zero angles.

TABLE 2

Interfacial contact angle data for untreated galena by the pressure of displacement method

$t = 25^{\circ}\text{C.} \pm 0.10^{\circ}$; galena A ($r = 8.18 \times 10^{-4}$ cm.)

LIQUID	DISPLACE- MENT PRESSURE	$S_{n3} \cos \theta_{n3}$	θ_{n3}	$\cos \theta_{n3}$ (K_{n3})	A_{1n}
Water advancing					
					dynes per cm.
<i>n</i> -Butyl acetate.....	-16.2	-6.52	119.7°	-0.495	65.2
Benzene.....	-41.9	-16.8	119.6°	-0.494	75.5
α -Bromonaphthalene.....	-51.0	-20.6	119.5°	-0.493	79.3
Average.....			119.6°	-0.494	
Water receding					
<i>n</i> -Butyl acetate.....	30.1	12.1	23.5°	0.917	
Benzene.....	75.5	30.3	27.0°	0.891	
Average.....			25.3°	0.904	

finely ground galena was used, which had been graded through sieves between 250 and 300 mesh. The graded galena was first shaken with acetone to remove possible traces of oils, etc., dried, then thoroughly mixed in a rotating cylinder.

The following table shows the treatments to which the various samples of the graded galena powders were subjected:

Sample	Treatment
Galena A.....	No further treatment
Galena B.....	Heated in air for 2 hours at 180–190°C.
Galena C.....	Heated in air for 4 hours at 180–190°C.
Galena D.....	Heated in air for 8 hours at 180–190°C.
Galena E.....	Heated in air for 24 hours at 180–190°C.

TABLE 3

Interfacial contact angle data for galena A heated in air at 180–190°C. for different lengths of time; pressure of displacement method (water advancing)

$$t = 25^{\circ}\text{C.} \pm 0.10^{\circ}; r = 8.18 \times 10^{-4} \text{ cm.}$$

LIQUID	DISPLACEMENT PRESSURE	θ_{1n}	$S_{n3} \cos \theta_{n3}$	θ_{n3}	$\cos \theta_{n3}$ (K_{n3})	A_{1n}
Heated 2 hours = galena B						
						<i>dynes per cm.</i>
Benzene.....	−33.0	0°	−13.3	113.0°	−0.390	74.0
α -Bromonaphthalene.....	−42.2	0°	−16.9	114.0°	−0.407	77.6
Average				113.5°	−0.398	
Heated 4 hours = galena C						
Benzene.....	−24.2	0°	−9.71	106.6°	−0.286	71.4
α -Bromonaphthalene.....	−30.4	0°	−12.2	107.0°	−0.290	73.9
Average				106.8°	−0.288	
Heated 8 hours = galena D						
Benzene.....	−17.1	0°	−6.87	101.7°	−0.202	69.6
Heated 24 hours = galena E						
Benzene.....	−10.9	0°	−4.38	97.4°	−0.129	68.6

EXPERIMENTAL

In the course of this investigation four different methods for measuring the angle of contact were used, namely: (a) a pressure of displacement method; (b) a horizontal plate method; (c) a vertical rod method; and (d) a deposited film method. In the following section these four methods, together with the apparatus and its manipulation, will be discussed.

(a) *Pressure of displacement method for the measurement of contact angles*

The pressure of displacement method used was that described by Bartell and Walton (4). Both the advancing and receding contact angles

were determined for the different galena–water–air systems and the different galena–water–organic liquid systems. The results obtained for the former systems are given in table 1, and for the latter systems in tables 2 and 3. The cosines of the different contact angle values galena–water–air (i.e., $\cos \theta_{13}$ values) are plotted against adhesion tension values (A_{13}) in the wetting characteristics graph in figure 1, and the cosine of the interfacial contact angle values (i.e., $\cos \theta_{n3}$ or K_{n3} values) are plotted against adhesion tension values in figure 2.¹

The adhesion tension values, A_{1n} , for the organic liquids against the different galenas were calculated from the advancing galena–water–air

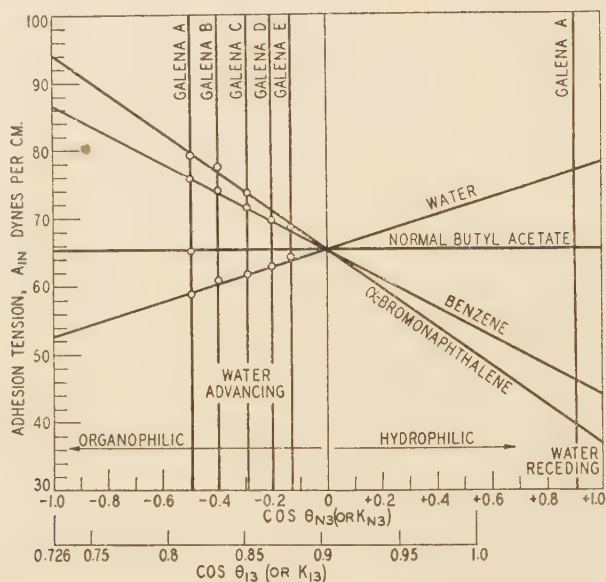


FIG. 2

and galena–water–organic liquid contact angle values from the equation $A_{13} - A_{1n} = S_{n3} \cos \theta_{n3}$ (3). The results were found to be in agreement with the linear relationship noted for similar systems by Bartell and Bartell (1). The effect of the heat treatment was similar in nature to that observed by Bartell and Walton (4) for stibnite, the powder becoming less organophilic the longer the period of heating.

¹ The adhesion tension versus $\cos \theta_{n3}$ or K_{n3} values shown in figure 2 were plotted according to the relationship observed by Bartell and Bartell (1) and were determined by their empirical equations: $m_n = 12.8 - S_{n3}$ (where m_n is the slope of the organic liquid line and S_{n3} the interfacial tension water–organic liquid), and equation $A_{1n} = m_n K_{n3} + 65.2$ (where A_{1n} = adhesion tension of the organic liquid against the solid of corresponding K_{n3} value). The position of each solid on the horizontal axis (i.e., the wetting characteristics value) was determined from the galena–water–organic liquid systems, being the average of the cosines of the interfacial contact angles.

It will be noted that according to the advancing angles all the samples are organophilic in nature, while according to their receding angles they are all hydrophilic. It will be noted also that all the advancing interfacial angles for a given sample of galena give the same value. Likewise all the receding values are practically the same.

From the above discussion it is evident that galena, from the standpoint of its wetting characteristics, acts as two different solids depending upon whether or not it is wetted with water. Thus the pressure of displacement method quantitatively confirms the qualitative tests, previously cited, regarding the wetting characteristics of galena.

The values obtained for galena by the pressure of displacement method were duplicable to within ± 2 per cent. This deviation was slightly greater than that which has previously been found for the method (± 1 per cent), the cause lying in the nature of the solid.

If we have a water-organic liquid interface in a membrane composed of galena powder, neither liquid will displace the other until a definite pressure is applied, the pressure necessary to cause the water to displace the organic liquid corresponding to the advancing contact angle value, and that necessary to cause the organic liquid to displace the water corresponding to the receding contact angle value. The system is apparently stable anywhere between these two limits. If, at any time in the course of the determination, the pressure falls to a value between those corresponding to the advancing and the receding contact angles, the pressure will remain at this value, there being no tendency for the interface to move and build up the pressure.

Since there was reason to believe that the surface of the original finely divided particles of powder might have been altered during their preparation (i.e., oxidized during the processes of grinding, sieving, and mixing), it was decided to attempt to obtain a fresh non-worked and non-oxidized surface. Crystals of galena were therefore cleaved, and measurements were made of angles formed by drops of water upon the cleaved surface. This method will be referred to as the horizontal plate method.

(b) Horizontal plate method for the measurement of angles of contact

This method consisted essentially in measuring the dimensions of small drops of a liquid resting upon a plane solid surface. Since small drops are approximately segments of spheres, the angle of contact may be calculated from their height and diameter, using the following equation:

$$\tan \frac{\theta}{2} = \frac{h}{r}$$

where h is the height of the drop, and r is the radius of the drop.

A freshly cleaved surface of the solid was placed in a small covered absorption cell having plane glass sides, the atmosphere within the cell having previously been saturated with the liquid the contact angle of which was to be measured. A small drop of the liquid was then introduced upon the surface of the solid. The height and diameter of this drop were measured by means of a cathetometer. The direction of motion of the liquid (i.e., advancing or receding) was controlled by adding or withdrawing liquid from the drop. One set of representative results is given in table 4.

Each of the determinations gave a zero receding water-air angle, but the finite advancing values were very erratic and varied by as much as 30°. The cause for this variation, we believe, lies in the methods used for introducing the liquid drop onto the solid surface. Several different methods were tried, the drop being added by means of a glass rod, a small glass pipet, and from a paraffin-coated rod, but none proved entirely satisfactory. It is almost impossible to place a liquid drop upon the solid

TABLE 4
Contact angle data for water upon freshly cleaved galena surfaces by the
horizontal plate method
 $t = 25^{\circ}\text{C.} \pm 1.0^{\circ}$

EXPERIMENT	θ_{13} (ADVANCING)	θ_{13} (RECEDING)
1	76°	0°
2	80°	0°
3	90°	0°
4	57°	0°
5	67°	0°

by means of a pipet or rod, and remove the pipet or rod without causing some vibration during the process. This vibration will cause the drop momentarily to flatten, the result being that the angle will exceed the advancing value and spreading will occur. Since this system is apparently stable with contact angles anywhere between the characteristic advancing and receding values, it will remain at an intermediate value. Some of the liquid is very apt to adhere to the rod or pipet upon its removal, and this also may cause the angle to be lower than the true advancing value. In spite of the common usage of this method, the importance of these sources of error has not been sufficiently stressed and different investigators have failed to take them into consideration, the result being that their advancing contact angle values have been too low.

The results of these measurements led us to believe that were it possible to cause the line of contact to advance slowly or recede slowly, one might obtain definite and characteristic values. Accordingly, the vertical rod method (2) was next tried.

(c) *Vertical rod method for the measurement of angles of contact*

A small freshly cleaved rod of the solid (approximately $3.0 \times 3.0 \times 12.0$ mm.) was held in a vertical position in such a manner that it could be slowly raised or lowered. The rod was carefully adjusted to such a position that two of its sides were parallel to the plane of light entering the camera. The rod was then slowly lowered until it extended through the liquid surface, the liquid being contained in a small glass absorption cell having parallel plane sides, and the line of contact of the liquid surface with that of the rod was photographed. The advancing liquid-air contact angle was measured from the resulting photographic plate. The rod was then slowly raised until the liquid gradually receded from its surface, and the receding liquid-air contact angle thus formed was photographed.

TABLE 5

Contact angle data for galena by the vertical rod method; alteration of surfaces by heating in air

$t = 25^\circ\text{C.} \pm 1.0^\circ$; time of heating = 1 hour

SAMPLE	TEMPERATURE OF HEATING	θ_{13}	$\cos \theta_{13}$	K_{a3} (CALCULATED)	A_{13}
	<i>degrees C.</i>				<i>dynes per cm.</i>
Galena F (untreated).....	25	90°	0.0	-5.09	0
Galena G.....	100	78°	0.21	-3.9	15.1
Galena H.....	200	53°	0.60	-1.7	43.4
Galena I.....	300	32°	0.85	-0.33	61.3
Galena J.....	400	24°	0.91	0.03	65.6
Galena K.....	500	0°	1.0	>0.54	>72.1

The value of the advancing water-air contact angle obtained with this method was 90° ($\cos \theta_{13} = 0$), and the value of the receding angle was zero ($\cos \theta_{13} = 1$). Since the advancing water-air angle obtained by this method was much larger than that obtained by the displacement pressure method, tests were carried out on cleaved rods which had been heated at given temperatures for definite periods of time. The results obtained with such rods are given in table 5.

The data obtained have been placed upon the graph in figure 1 (according to Bartell and Bartell (1)). It will be noted that the wetting characteristics were greatly altered by the heat treatment, passing from the strongly organophilic condition ($\cos \theta_{13} = 0$) to progressively lesser organophilic conditions and finally to what appears to be a definitely hydrophilic condition.

The contact angles measured upon freshly cleaved galena surfaces by the vertical rod method were duplicable to within $\pm 3^\circ$. The advancing

water-air angles of contact upon the heat-treated galena rods were considerably less duplicable, the cause apparently lying in the uneven alteration of the surface of the rods.

The results with the vertical rod confirmed our earlier views that failure to obtain definite and reproducible values with the horizontal plate method was caused by our inability to alter gradually the solid-liquid-air point of contact. Better control of the drop on the plate could be obtained by bringing the liquid through a hole in the plate, causing the drop to expand or contract. Since the drilling of galena plates offered some difficulty, and inasmuch as it is rather difficult to obtain perfectly smooth and plane surfaces by the cleavage of crystals, a method was devised which enabled us to accomplish the objectives mentioned above. This method will be referred to as the deposited film method.

(d) Deposited film method for the measurement of angles of contact

Numerous investigators have obtained mirror surfaces of various substances by slowly distilling the material in a high vacuum and condensing it upon the object it is desired to coat. We have employed this method in the preparation of surfaces for contact angle measurements.

In recent years considerable work has been carried out on the structure of deposited films. Finch and Quarrell (7) found that very thin films showed a distortion of crystal units, these tending to fit the lattice of the material of the base upon which they were deposited. They found the crystal structure of thicker films to be normal, the surface having a random orientation unless heated. In such a case orientation occurred. Dixit (6) found the orientation to be independent of the nature of the base, provided its surface was smooth and amorphous. This work appears to show that freshly deposited surfaces should be ideal for our purpose, provided the film is deposited upon a smooth and amorphous base.

The substance to be studied was deposited upon a polished glass surface having a small hole through the center (i.e., a tip, see figure 3). A drop of the liquid, the contact angle of which was to be measured against this solid, was introduced onto the surface by forcing the liquid up through the hole, and the angle of contact formed was then photographed. By proper manipulation of the apparatus both advancing and receding angles could be measured.

The method used in measuring the angles formed upon these deposited surfaces was a modified horizontal plate method. The arrangement for running the liquid out onto the plate permitted accurate control of the movement of the drop. Moreover, the system was comparatively free from vibration. In order to insure true advancing and receding values, the angle was photographed while the liquid was moving very slowly. The surface of the solid must not be in an inverted position if materials

giving an angle greater than 90° are used, as in such a case the drop advances to approximately 90° , elongates, and then falls off.

Data for advancing and receding water-air angles upon these different deposited films are given in table 6. It will be observed that the water-

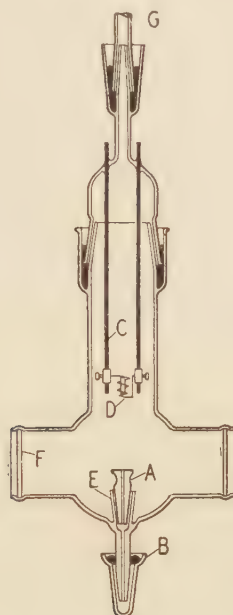


FIG. 3. APPARATUS FOR THE MEASUREMENT OF ANGLES OF CONTACT IN AN INERT ATMOSPHERE BY THE DEPOSITED FILM METHOD

A, tip; B, cap and seal; C, tungsten leads; D, heating coil; E, tip support; F, plane glass windows; G, vacuum outlet.

TABLE 6
Contact angle values of water upon deposited films
 $t = 25^\circ\text{C.} \pm 1.0^\circ$

MATERIAL	θ_{13} (ADVANCING)	θ_{13} (RECEDING)
Lead sulfide.....	90°	0°
Arsenious sulfide.....	97°	0°
Bismuth.....	110°	0°
Sulfur.....	98°	66°
Biphenyl.....	107°	35°
Naphthalene.....	103°	35°

air contact angles formed upon galena surfaces were the same as those which were found by the rod method, using freshly cleaved, unheated galena.

The angles of contact measured by this method were duplicable to within $\pm 3^\circ$. The method has a very wide range of applicability. Other investigators have used the vacuum sublimation process for the preparation of mirror surfaces of practically all of the metals, a large number of salts, and several oxides. Our own work has indicated that many sulfides and organic materials would give good mirror films. Results obtained for some of these systems are given in table 6. The method should also be applicable to materials which are very readily oxidized by exposure to the atmosphere, as slight modifications in the design of the apparatus would allow the determination of contact angles upon these deposited films to be carried out in an inert atmosphere, or even *in vacuo* (see figure 3). Work is being extended along this line.

We believe that the process for preparing fresh mirror surfaces of various solids by sublimation of the material *in vacuo* could be advantageously used in the preparation of surfaces for the measurement of contact angles by other methods.

DISCUSSION OF METHODS AND RESULTS

A study of the methods used in this investigation for the measurement of contact angles reveals that each of the methods may be satisfactory for certain systems.

The pressure of displacement method gives duplicable and apparently significant results. It is the only method suitable for use with powdered materials. In case the surface properties of a solid become altered in the process of pulverization (which may sometimes be the case), this method obviously would not give values characteristic of an uncontaminated surface of the pure substance.

The horizontal plate method as generally employed is suitable for use with certain substances, but not for substances which give dual contact angles (advancing and receding angles), each of which is apparently stable, unless some means is employed to control very accurately the spreading of the drop.

The vertical rod method appears to give reliable results with those substances which will give clean smooth surfaces of proper shape.

The deposited film method is primarily suited for the determination of angles of contact upon pure materials, films of which can be formed by sublimation. This method offers greatest possibilities in fundamental studies of pure and uncontaminated surfaces.

Results obtained with the vertical rod method and with the deposited film method indicated that with a strictly clean galena surface the galena-water-air advancing contact angle is one of 90° , and that the receding angle is zero.

Results obtained using powdered galena and the pressure of displace-

ment method indicated that the surface of the powdered galena used was less organophilic than was that of the freshly cleaved or freshly sublimed galena used in the vertical rod method and in the deposited film method. By heat treatment the galena used in the vertical rod method could be caused to approach in surface properties the powdered galena. In these cases it is believed the change in surface properties was caused by oxidation.

A study of all the results obtained with galena indicates that this solid has surface properties quite different from other solids previously studied by us (as carbon and silica), in that it gives widely different and apparently stable advancing and receding contact angles and in so doing appears to function either as an organophilic or as a hydrophilic solid depending upon whether it is first wetted by an organic liquid or by water. From data given in table 6, obtained with the film method, it appears probable that other substances will be found to possess properties similar to those exhibited by galena.

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